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KINETICS OF REACTION BETWEEN PURE AND Fe_2O_3 CONTAIN-
ING NaCl OR CaCl_2 WITH A GAS PHASE OF SO_2 , O_2 AND SO_3

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KINETICS OF REACTION BETWEEN PURE AND Fe_2O_3 -CONTAINING NaCl
OR CaCl_2 WITH A GAS PHASE OF SO_2 , O_2 and SO_3

[Zur Kinetik der Reaktion zwischen reinem und Fe_2O_3 -haltigem
NaCl oder CaCl_2 mit einer Gasphase aus SO_2 , O_2 und SO_3]

"
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Kinetics of Reaction Between Pure and Fe_2O_3 -Containing NaCl
or CaCl_2 with a Gas Phase of SO_2 , O_2 and SO_3

Summary

The velocity of formation of gaseous chlorine which results from the reaction of NaCl or CaCl_2 with gas mixtures of SO_2 - O_2 or SO_2 - O_2 - SO_3 has been measured. For mixtures of SO_2 - O_2 the reaction rate depends on the composition of the gas atmosphere at constant temperature. For concentrations of SO_3 above one percent, the rate velocity is determined only by the SO_3 concentration. Furthermore, the influence of admixtures of Fe_2O_3 on the kinetics of these reactions has been examined.

Chloridizing roasting of ores is used to convert metal oxides or sulfides into soluble or volatile compounds. [1, 2, 3] The process currently used to prepare pyrite cinders is designed to convert all nonferrous metals present in low concentrations into compounds soluble in water or acids, and to convert the iron present into an insoluble oxide. The necessary chlorine is supplied by the addition of NaCl.

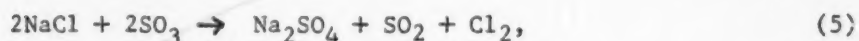
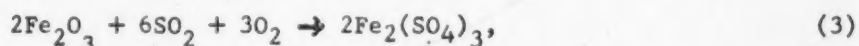
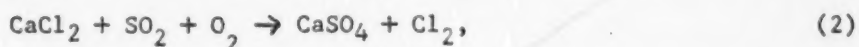
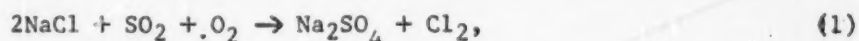
Various reactions take place during roasting, they overlap and influence each other. They are either solid phase reactions or heterogeneous reactions between solids and the gases present in the roasting atmosphere. [4] Gaseous chloride is released [5] by the chlorinating agent which, in turn, reacts with metal oxides, sulfides or sulfates to form metal chlorides.

The complex sequence of reactions has been subdivided into partial reactions in order to investigate the various processes occurring during chloridizing roasting [6, 7] most of which are largely unknown as yet. In

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the present study, the reactions of the NaCl and CaCl₂ chlorine vehicles with SO₂-O₂ gas mixtures have been examined in the temperature range of between 500 and 600°C, first with mixtures of changing composition and then with increased SO₃ content by measuring weight increases. Furthermore, the effect of admixtures of Fe₂O₃ on these reactions, and the behavior of pure Fe₂O₃ with the reaction gases has been examined.

Thermodynamic calculations show that the following reactions



may take place. Kinetic tests determine the speeds with which these reactions occur.

Test Arrangement and Execution

The reaction speed of pure and Fe₂O₃-containing NaCl or CaCl₂ and also of Fe₂O₃ with SO₂-O₂, mixtures with and without, a SO₃ content have been measured at temperatures of 500, 550 and 600°C. Weight increases of compacts have been determined with a spring scale and reaction speeds have been determined from these values in accordance with Eqs. (1) to (6). The details of the equipment used have been described in an earlier publication. [8]

The purest form of crystalline NaCl and analytically pure, fine-grained CaCl₂ [9], as well as Fe₂O₃ in the form of chemically pure

rouge [10] were used in the tests. Analysis of these substances confirmed the perfect composition of these substances. Compacts of 29 mm $\varnothing$ and a height of 1.1 - 1.6 mm were made from the pure or mixed substances of fine powdery consistency in a steel compacting mold and using a pressure of 3000 kgf/cm². They were subsequently sintered for one hour at 700°C after slow heating under nitrogen in order to increase compactness and density.

The geometric surface of each sample which was available for the reaction was calculated from the diameter and height of the compact. The calculated density of the sintered samples was 96% of the theoretical density. The pore volume present, therefore, is very low, so that the measured surface of the sample was taken as the reacting surface.

The effect of Fe₂O₃ admixtures was determined by the addition of 1 - 10% by weight of Fe₂O₃ to the pure, ground substances.

After individual tests, the samples were examined for any sulfate that might have formed. Determination was in accordance with the barium-chromate method. The amounts determined for SO₄ varied by no more than 3% from the values calculated for the formation of sulfates from the weight increases.

The N₂, SO₂ and O₂ gases used in the experiments were taken from steel containers. Speed and composition of the reaction gases were adjusted by means of calibrated capillary flow meters which had been filled with concentrated sulphuric acid. A flow rate of 48 Nl/h (liters per hour, under normal conditions) proved to be sufficiently high to assure that any transport process in the surrounding gaseous area had no influence on the reaction speed that was to be measured.

Dependency on gaseous composition was measured with pure oxygen and mixtures of 20, 40, 60 and 80 mol% SO_2 and corresponding parts of oxygen. Furthermore, the effect of an increasing part of SO_3 in the reaction gas was examined. To produce the SO_3 , a mixture of 50% SO_2 and O_2 each was passed through a contact furnace which contained platinum asbestos as catalyzer and was maintained at a temperature of 450°C , before the gas entered the reaction chamber. Measurements were conducted with contents of 1.4, 4.2, 7.1, 10.1 and 13.2 mol% of SO_3 .

Measurements Results

Weight increases of the samples determined in measurements of $\text{SO}_2\text{-O}_2$ mixtures result from the formation of sulfates according to total reaction (1) to (3) (thermodynamically possible). It was confirmed by the analytical determination of sulfate contents according to the barium chromate method. [11] The reaction of NaCl , CaCl_2 , Fe_2O_3 with an SO_3 -containing $\text{SO}_2\text{-O}_2$ mixture occurs according to total reactions (4) to (6) (thermodynamically possible), as could be established by a comparison of weight increases and analytical findings. The graphic

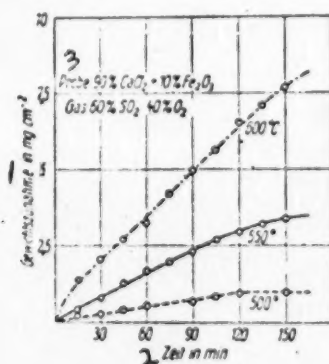


Figure 1. Weight increases of samples relative to time
1 - weight increase in $\text{mg}\cdot\text{cm}^{-2}$; 2 - time, in minutes; 3 - sample,
90% CaCl_2 + 10% Fe_2O_3 gas, of 60% SO_2 + 40% O_2 .

representation of weight increases per cm^2 of sample surface in relation with time is illustrated by the curve in Figure 1, which is typical for all the reactions examined.

The curves for pure substances and those with admixtures of 1 or 10% of Fe_2O_3 , which are similar for all measurements, show three sections:

(a) after an initial starting time, a constant speed is reached after the test has run for 10-20 minutes;

(b) the linear section of equally fast reaction extends to about 100 minutes under existing test conditions for $\text{SO}_2\text{-O}_2$ mixtures and 5 - 25 minutes of testing time for mixtures with the addition of SO_3 . Reactions of the order of 0 appear in this range of linear time dependence. Reaction partners are present in sufficient and constant amounts at the reaction site, and the unhindered chemical process determines the speed.

This section of the curve was used for calculating reaction rate constants;

(c) the reaction slows down because the developing layer of solid reaction product begins to exert its influence.

The increase of the linear portion of the weight increase corresponds to a constant, k , which is characteristic for the reaction rate under existing conditions. In general, the values of this reaction rate constant increases as temperature increases. If these values are plotted at a constant temperature in dependence on the composition of the gas, the values for NaCl and CaCl_2 of approximately the same order of magnitude result in asymmetrical curves which show a maximum at approximately 20 mol% SO_3 and 30 mol% O_2 , as illustrated in Figures 2 and 3. No reactions are recorded for pure NaCl and CaCl_2 with SO_2 and O_2 gases in pure form,

so that the curves approach 0. Dependence of the gaseous composition shows a similar asymmetrical development for samples with Fe_2O_3 content as was found for pure NaCl and CaCl_2 , whereby the maximum at about 20 mol% SO_2 is more clearly apparent. No reaction was found for oxygen alone. In contrast, specific reaction rate values could be measured for SO_2 at temperatures above 550°C .

Specific reaction rates for pure Fe_2O_3 recorded in Figure 4 show a different reaction; they are higher and increase with increasing SO_2 content. Tests with oxygen alone again showed no reaction. However, a high specific reaction rate was found with SO_2 alone.

The concentration of SO_3 that had formed as a result of reaction (4) was established by an analysis of the gas. Amounts were found for pure NaCl and CaCl_2 which correspond to 0.01 - 0.07 mol% of the reaction gas. The values for Fe_2O_3 are 0.1 - 0.55 mol% SO_3 . The amount of SO_3 increases

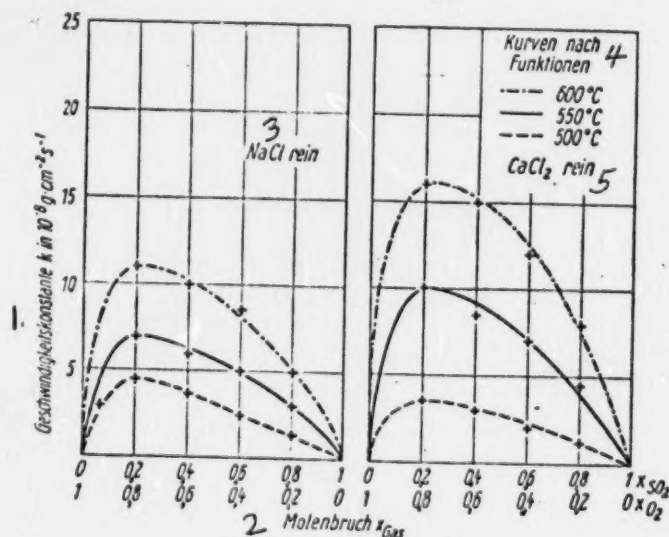


Figure 2. Dependence of the specific reaction rate, k , on the composition of the gaseous mixture for the reaction of pure NaCl , or CaCl_2 with SO_2 - O_2 mixtures (curves calculated according to equations (10) and (11))

1 - specific reaction rate in $10^{-8} \text{ g} \cdot \text{cm}^{-2} \text{ s}^{-1}$; 2 - mole fraction; 3 - NaCl pure; 4 - curves according to functions; 5 - CaCl_2 pure.

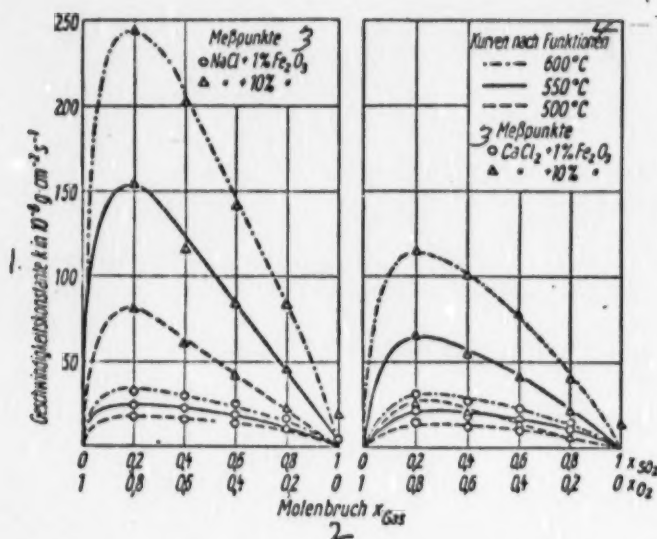


Figure 3. Dependence of the specific reaction rate, k , on the composition of the gaseous phase for the reaction between NaCl containing Fe_2O_3 admixtures or CaCl_2 with $\text{SO}_2 - \text{O}_2$ mixtures (curves calculated according to equation (13)).

1 - specific reaction rate, k , in $10^{-8} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$; 2 - mole fraction; 3 - points measured; 4 - curves according to functions.

in all cases as the content of SO_2 in the reaction gas increases and as the content of Fe_2O_3 in the sample increases.

In mixed samples consisting of NaCl or CaCl_2 with 1% Fe_2O_3 , 0.02 - 0.12 mol% of SO_3 were found in the gas; in samples consisting of NaCl and 10% Fe_2O_3 , 0.1 - 0.6 mol% SO_3 were found, and in samples consisting of CaCl_2 with 10% Fe_2O_3 , 0.1 - 0.3 mol% SO_3 were found.

The specific reaction rates increase with increasing SO_3 admixture to the reaction gas. Specific reaction rates for CaCl_2 increase with higher temperatures, as usual. However, an apparent decrease is found for NaCl. This reaction of all NaCl-containing substances towards SO_3 indicates that a secondary reaction takes place which does not permit comparison of the results from these measurements.

Evaluation of the Test Results

The sequence of heterogeneous reactions as found in the tests carried out by us can be arranged into the following phases:

- A. transporting the reaction partners to the site where the reaction will take place;
- B. adsorption on the surface of the solid substances;
- C. chemical reaction on the phase threshold;
- D. desorption;
- E. transporting the reaction products away from the site where the reaction took place.

A stationary condition was achieved during measurements as a result of the high flow rate of reaction gas, so that the gas chamber was free of any effects from the process of transporting. Thus, the speed of the reactions is determined by one of steps B, C or D.

A reaction between gas and solid phase is triggered by collision exchange which results in the reaction via adsorption or chemisorption. Adsorption plays an important role in the process, as shown by the present findings. It consists of an interaction between gas molecules and solid molecules, which ranges from physical adsorption, characterized by the weak Van der Waal's forces, to chemisorption, whose forces are already similar to those of chemical bonding. At the high temperatures used in the present tests, chemisorption occurs to an increasing degree.

The curves illustrated in Figures 2 and 3 can be expressed by an equation which contains one expression for the adsorption of each of the two gases. [6, 7]

$$k = C \frac{x_{SO_2}}{a + x_{SO_2}} \cdot \frac{x_{O_2}}{b + x_{O_2}} \rightarrow C \cdot A \cdot B \frac{x_{SO_2}}{1 + A \cdot x_{SO_2}} \cdot \frac{x_{O_2}}{1 + B \cdot x_{O_2}}$$

Mole fraction times the respective gas is used as measure of concentration. The two constants, a and b, must be determined empirically and result in the assymetrical development of the curve as a result of their differences in size.

The values measured, and, hence, the dependence of the specific reaction rate, k, on the composition of the gas are characterized suitably with $a = 0.01$ ($A = \frac{1}{a} = 100$) and $b = 0.4$ ($B = \frac{1}{b} = 2.5$) for NaCl and $CaCl_2$, in the range of temperatures used in the tests. The temperature-dependent constants C are determined according to the compensation on theorem.

Specific reaction rates for Fe_2O_3 are greater by a factor of about 100, as shown in dependence on the mole fraction x_{SO_2} in Figure 4.

The values measured and, thus, the dependence of k alone on the SO_2 concentration in the reaction gas can be expressed by a simple linear equation.

$$k = D \cdot x_{SO_2} \quad (9)$$

for the temperature range tested, where x_{SO_2} stands for the mole fraction of SO_2 and D is a temperature-dependent constant.

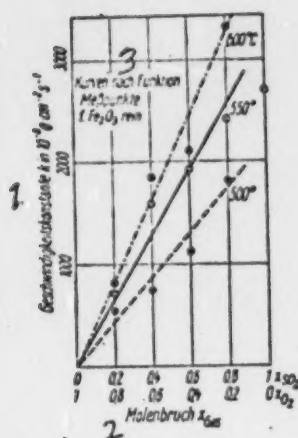


Figure 4. Dependence of specific reaction rate, k , on the composition of the gaseous phase for the reaction of Fe_2O_3 with SO_2 - O_2 mixtures (curve calculated according to equation (12)).

1 - specific reaction rate, k , in $10^{-8} \text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$; 2 - mole fraction x_{gas} ; 3 - curves according to the function of points measured for Fe_2O_3 , pure.

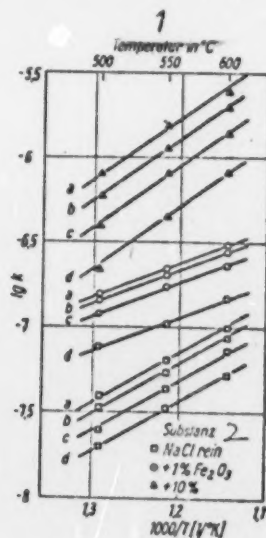


Figure 5. Dependence of specific reaction rate, k , in $\text{g}/\text{cm}^2 \cdot \text{sec}$ on temperature for the reaction of NaCl with SO_2 - O_2 mixtures.

- a) 20 mol% SO_2 - 80 mol% O_2
- b) 40 mol% SO_2 - 60 mol% O_2
- c) 60 mol% SO_2 - 40 mol% O_2
- d) 80 mol% SO_2 - 20 mol% O_2

1 - temperature, $^{\circ}\text{C}$; 2 - substance $\square$ - NaCl , pure.

The dependence of the specific reaction rate on temperature can be determined by means of the calculations according to Arrhenius. The plotting of $\log k$ against $\frac{1}{T}$ shows largely a parallel development of the straight line for each substance, as is illustrated for NaCl in Figure 5. The apparent activation energy, E , of the reaction can be determined from the rise of the curve.

The functions for the reaction with SO_2 - O_2 mixtures are for pure NaCl:

$$i = 3.78 \cdot 10^{-4} \cdot e^{-13,500/RT} \cdot \frac{x_{\text{SO}_2}}{0.01 + x_{\text{SO}_2}} \cdot \frac{x_{\text{O}_2}}{0.4 + x_{\text{O}_2}} \quad (10)$$

for pure CaCl_2 :

$$i = 1186.7 \cdot 10^{-4} \cdot e^{-22,500/RT} \cdot \frac{x_{\text{SO}_2}}{0.01 + x_{\text{SO}_2}} \cdot \frac{x_{\text{O}_2}}{0.4 + x_{\text{O}_2}} \quad (11)$$

for pure Fe_2O_3 :

$$i = 56.2 \cdot 10^{-4} \cdot e^{-8,500/RT} \cdot x_{\text{SO}_2} \quad (12)$$

The addition of Fe_2O_3 to NaCl and CaCl_2 results in an increased acceleration of sulfate formation the greater the admixture of Fe_2O_3 . The dependence of specific reaction rate, k , on the composition of the reactive gas develops in a form similar to the asymmetrical course established for pure NaCl and CaCl_2 . The same function represents the different curves, the exception being that the constants have to be adjusted in accordance with the values recorded in Table 1.

The change of the constants in accordance with temperature for 10% Fe_2O_3 admixtures corresponds to the properties of exothermal adsorption;

the values for b become so great that $B = \frac{1}{b}$ approaches 0 and the dependence of the concentration of O_2 becomes linear as a result.

The equation is as follows:

$$k = C \cdot \frac{x_{SO_2}}{a + x_{SO_2}} \cdot x_{O_2} = C_0 \cdot e^{-E/R \cdot T} \cdot \frac{A \cdot x_{SO_2}}{1 + A \cdot x_{SO_2}} \cdot x_{O_2} \quad (13)$$

Constants for adsorption demonstrate that SO_2 is adsorbed considerably more than O_2 . This corresponds to the familiar phenomenon that adsorption of gases increases with a higher boiling point.

In the reactions examined between $NaCl$ and $CaCl_2$ and SO_2 - O_2 mixtures a preferential absorption of the more easily adsorbed reaction gas SO_2 will take place.

O_2 , the component of lower adsorption properties, will be adsorbed only at a higher concentration which corresponds to the composition of the gas at the maximum of about 20 mol% SO_2 - 80 mol% O_2 , and will be reactive to a considerable degree, so that the most favorable mole ratio for the reaction of $SO_2:O_2$ is reached in the adsorption layer. In this case, the sulfate complex forms with a relative high rate of speed. A slowdown in the reaction rate will result for lower or higher SO_2 contents because either too little SO_2 or O_2 are available in the reaction chamber.

The differences in adsorption found for the two gases are demonstrated in Figure 6, in which the expression for the Langmuir adsorption isotherm is plotted in dependence on the mole fraction, x , with the adsorption constant established for each gas.

Table 1

Apparent Activation Energy Factors and Adsorption Constants for the Reaction of NaCl and CaCl₂ with SO₂-O₂ Mixtures

	NaCl		CaCl ₂		Pure	+10% Fe ₂ O ₃	+1% Fe ₂ O ₃	+10% Fe ₂ O ₃	Fe ₂ O ₃
	Pure	+1% Fe ₂ O ₃	Pure	+1% Fe ₂ O ₃					
E kcal/mol	13.5	9.0	22.5	11.5	22.5	22.0	22.0	22.0	8.5
C ₀ or D ₀	3.78·10 ⁻⁴	1.12·10 ⁻⁴	1186.7·10 ⁻⁴	4.65·10 ⁻⁴	1186.7·10 ⁻⁴	6710·10 ⁻⁴	6710·10 ⁻⁴	56.2·10 ⁻⁴	
A = 1/a	100	66.7	100	66.7	100	500 50	550 20	600 12.5	(0)
B = 1/b	2.5	1.5	2.5	1.5	2.5	-	-	-	-

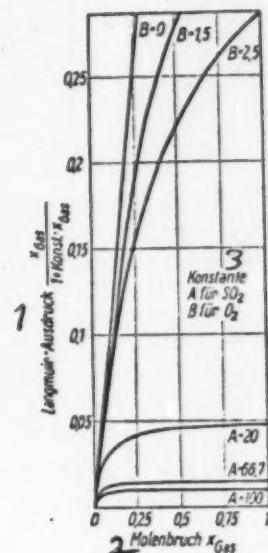


Figure 6. Effect of the adsorption constants measured on the Langmuir adsorption isotherm in dependence of gas concentration.

1 - Langmuir formula

$$\frac{x_{\text{gas}}}{1 + \text{const.} \cdot x_{\text{gas}}};$$

2 - mole fraction x_{gas} ; 3 - constant A for SO₂ B for O₂.

Accordingly, SO_2 ($A = 20-100$) is adsorbed almost to the saturation point and coating density, O , is between 0.80 and 0.99. In contrast, adsorption of O_2 ($B = 0-2.5$) still corresponds to the rising portion of the adsorption isotherm, its coating density reaches a maximum of 0.69. This observation applies to the present case of mixture adsorption, in which the gases have a mutual effect on each other.

The different behavior of the reaction of pure Fe_2O_3 with reaction gases is demonstrated by another type of function. Because a very strong reaction was only found for SO_2 as reactive gas, the hypothesis is not applicable here that mutual adsorption is again decisive just as it is for NaCl and CaCl_2 . The addition of SO_2 to Fe_2O_3 , which is known from the SO_3 contact process must be assumed to be the primary process which leads to the intermediate products of FeSO_4 and FeO ^[12]. This process has to be regarded as chemisorption of SO_2 . Then the conversions of the iron compounds and the oxidizing effect of O_2 follow as secondary reactions, which result in the formation of $\text{Fe}_2(\text{SO}_4)_3$. The greater the amount of chemisorbed SO_2 , which depends on the concentration present in the gas, the stronger is the reaction. The accelerated reaction of NaCl ^[13] and CaCl_2 resulting from increased additions of Fe_2O_3 develops parallel to a decrease of the adsorption constant in the functions. Probably, the adsorption equilibrium of the gases is interfered with by Fe_2O_3 and shifted in the direction of a greater consumption for the formation of sulfates. Despite an apparent lower adsorption, this results in a higher reactivity with the reaction gases, which results in increase of the specific reaction rates by up to 20 times their original figure.

On the basis of the strong interaction of Fe_2O_3 with SO_2 , the former will act as transmitter of reactive SO_2 , or as catalyzer for the formation

of SO_3 in the adsorption layer and will, thereby, enable the reaction of NaCl and CaCl_2 to take place at a more rapid rate. Again, the optimum ratio of composition is found to lie at 20 mol% SO_2 - 80 mol% O_2 of the gases in the adsorbed layer, which results in a maximum formation of sulfate as a consequence of the accelerated reaction caused by Fe_2O_3 . In addition, a reaction of solid substances will occur increasingly as a result of the admixture of Fe_2O_3 which leads to an exchange between ions of the iron sulfate which forms, and the NaCl or CaCl_2 , which is indicated by deposits of small amounts of FeCl_3 at cold locations in the measuring apparatus [14].

The rate of the phase limit reaction is measured in the test range of linear time dependence. In the measuring range up to 30% of reaction, no influences can be found which results from the products that form.

No effect of SO_3 on the formation of sulfate can be found for a percentage of SO_3 which has been established to be 0.6%. The maximum for the homogeneous formation of SO_3 lies at 60-80 mol% SO_2 in the reaction gas, while the maximum of the reaction rate is measured at 20 mol% SO_2 . The concentration of the SO_3 which has formed as a result of the homogeneous reaction and at active points (Fe_2O_3) is too low to displace the reaction mechanism in the adsorption layer. Studies in which 1.4-13.2 mol% SO_3 were added to the SO_2 - O_2 mixtures showed that the reaction rate is considerably increased with increasing SO_3 admixtures.

When SO_2 is used, the admixture of 1 or 10% Fe_2O_3 to NaCl or CaCl_2 will accelerate the reaction merely by the factor of about 2.

Since it can be expected that the first step of the heterogeneous reaction is an adsorption of the gas on the surface of the solid substance, even in reactions with the use of SO_3 , the dependence of the specific reaction rate on SO_3 concentration can be expressed in the form of an equation for this adsorption. The potential function corresponding to this adsorption isotherm which states that

$$k = k_0 \cdot e^{-A/RT} \cdot x_{\text{SO}_3}^{1/n} \quad (14)$$

can be used to express the course of the measured points in a suitable manner.

In equation (14), k_0 is the specific reaction rate, A the activation energy, R the general constant of the gas, T is the absolute temperature, x_{SO_3} is the mole fraction of SO_3 , and $1/n$ is a constant factor which indicates the degree of adsorption. Although the factors $1/n$ that were measured exhibit a slight dependence on temperature, it cannot be recorded accurately under the existing test conditions. After temperature dependence has been established, the following laws on the reaction rate can be formulated:

pure CaCl_2 :

$$i = 16033 \cdot 10^{-4} \cdot e^{-20,500/RT} \cdot x_{\text{SO}_3}^{0.6} \quad (15)$$

99% CaCl_2 + 1% Fe_2O_3 :

$$i = 77.8 \cdot 10^{-4} \cdot e^{-10,500/RT} \cdot x_{\text{SO}_3}^{0.7} \quad (16)$$

90% CaCl_2 + 10% Fe_2O_3 :

$$i = 47.5 \cdot 10^{-4} \cdot e^{-9,000/RT} \cdot x_{\text{SO}_3}^{0.7} \quad (17)$$

pure Fe_2O_3 :

$$i = 48.1 \cdot 10^{-4} \cdot e^{-7,500/RT} \cdot x_{\text{SO}_3}^{0.45} \quad (18)$$

Figures 7 and 8 show the dependence of the specific reaction rate for CaCl_2 and Fe_2O_3 in dependence on the mole fraction x_{SO_3} .

The temperature dependence was used as parameter. The curves have been calculated according to Eqs. (15) to (18). No useful results were found for the measurements with NaCl because pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$) is formed in addition to sulfate [5, 15, 16] which makes it impossible to properly weigh and evaluate the findings.

There is no formation of addition compounds or polysulfates with CaCl_2 . The reaction between SO_3 in the adsorption layer and the Cl -ions at the surface determines the reaction rate, which is lower than that for NaCl . Probably, the highly symmetrical cubic lattice of NaCl is far more suitable for the addition of SO_3 than the tetragonal structure of CaCl_2 .

The reaction rate can be represented for admixtures of over 1 mol% as a function of the SO_3 concentration.

Despite the higher concentrations, no effect of SO_2 and O_2 can be found. [11] This results from the strong interaction between SO_3 and its reaction partner, which is a consequence of the tendency of SO_3 to form addition compounds. At concentrations of more than 1 mol%, SO_3 preferably aggregates on the surface of the solid substances, with the amount of adsorbed SO_3 depending on its concentration in the gaseous phase. It determines the speed with which sulfate is formed, which takes place quite easily due to the great forces of interaction.

The properties of the substances and SO_3 are approximately represented by the exponential factor $1/n$. As $1/n$ becomes smaller, the dependence of the

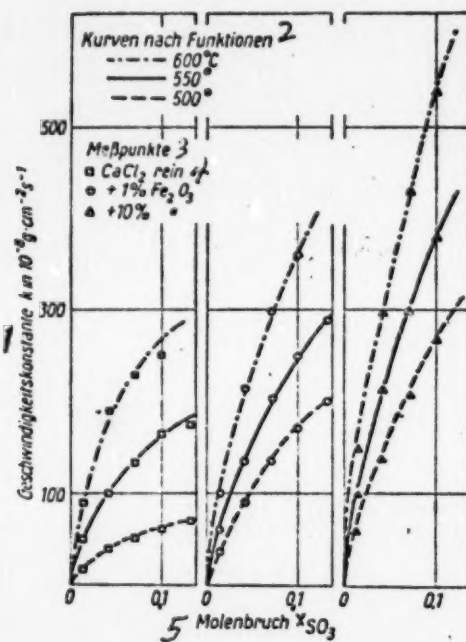


Figure 7. Dependence of the specific reaction rate, k , on the gas concentration for the reaction of CaCl_2 with an SO_2 - O_2 mixture containing SO_3 (curves calculated in accordance with Eqs. (15) to (17). 1 - specific reaction rate k in $10^{-8} \text{g.cm}^{-2} \text{sec}^{-1}$; 2 - curves according to functions; 3 - points measured; 4 - pure; 5 - mole fraction x_{SO_3} .

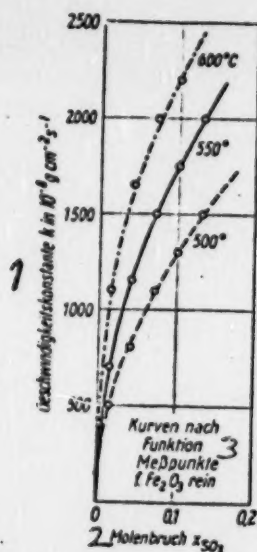


Figure 8. Dependence of specific reaction rate, k , on gas concentration for the reaction of Fe_2O_3 with an SO_2 - O_2 mixture containing SO_3 (curves calculated in accordance with equation (18)).
 1 - specific reaction rate k in $10^{-8} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$; 2 - mole fraction x_{SO_3} ;
 3 - curves according to the functions of points measured for Fe_2O_3 , pure.

gas concentration will approach a constant value and the adsorption of gas will become greater.

The exponential factor has the smallest value for Fe_2O_3 , which corresponds to a relatively high adsorption, and, hence, reaction. The higher exponential factors for $CaCl_2$ can be considered as signs of a relatively low adsorption and proportionally weaker reaction, which results in the lowest reaction rates.

The exponential factors become higher when Fe_2O_3 is added to the pure substances. Despite a lower adsorption, which probably results from the fact that its equilibrium has been shifted in favor of the

formation of sulfate, the rate of reaction is increased as much as three times.

The reaction of Fe_2O_3 with SO_3 takes place via chemisorption as simple addition and without any desorption of a gaseous reaction product. It proceeds with ease, as is generally known from this reaction of metal oxides with SO_3 .

The accelerated influence of the addition of Fe_2O_3 in the case of CaCl_2 will again be a result of the transference of reactive SO_3 and the reaction in the solid phase as a result of a transposition between ions of the developing iron sulfate and chloride.

The apparent activation energies occurring in the formation of sulfates with SO_2 are reduced if Fe_2O_3 is added, which indicates an easier formation of sulfate, facilitated by Fe_2O_3 , which is expressed in an accelerated rate of reaction. The lowest value established for pure Fe_2O_3 corresponds to a simple reaction by addition.

Discussion of the Results

A comparison of the reactions of SO_2 - O_2 mixtures with and without admixtures of SO_3 show the effects of the SO_3 . The reaction of NaCl to sulfate and polysulfate is considerably accelerated. The established increases in the rate of reaction for CaCl_2 to form sulfate lies at a factor of about 10. It becomes greater with increasing contents of SO_3 in the reaction gas.

The accelerating effect of Fe_2O_3 added to NaCl and CaCl_2 is marked for mixtures of SO_2 - O_2 , but is only slightly apparent for admixtures with SO_3 .

For the reaction of pure Fe_2O_3 , there is practically no change in the specific reaction rate with $\text{SO}_2\text{-O}_2$ alone or with additions of SO_3 .

The apparent activation energies of 7.5 - 22.5 kcal/mol lie within the range which is customary for heterogeneous reactions between solids and gases and usually become lower for reactions occurring at a higher rate of velocity.

The different effects of the Fe_2O_3 admixture to NaCl and CaCl_2 reacting to $\text{SO}_2\text{-O}_2$ gas mixtures with and without SO_3 lead us to conclude that the acceleration of the reaction is based on the formation of SO_3 within the adsorbed layer in which Fe_2O_3 acts as catalyzer. This explains why Fe_2O_3 is highly effective in the formation of sulfate from $\text{SO}_2\text{-O}_2$ via SO_3 while hardly any effect can be found for SO_3 contents that are present in the gas phase.

The behavior of SO_2 which is active only in the presence of O_2 , and the tendency to reach a higher form of oxidation, together with the great effect of SO_3 and the differences in effect for Fe_2O_3 lead us to the conclusion that the reaction usually develops via SO_3 when sulfates are formed from NaCl and CaCl_2 .

The composition of the layer of adsorption on the surface of the solid is decisive for the chemical processes that occur in the formation of sulfates. It depends on the differences in adsorptive power vis-a-vis the individual gases and on the concentration of the latter in the reaction gas. The dimensions and correlation of the adsorption constants established in the equations which have been formulated provide information on adsorption.

In the reaction of NaCl and CaCl₂ with SO₂-O₂ mixtures which contain SO₃ of less than 1 mol% as a result of a secondary reaction, the concentration of free SO₃ is too low to displace the reaction mechanism in the adsorbed layer of SO₂ and O₂. Their differences in adsorption are decisive for the reaction rate. For concentrations of SO₃ above 1 mol% (up to approximately 15 mol%), the layer of adsorption consists primarily of chemisorbed SO₃ as a consequence of the tendency of the SO₃ to form additive compounds, so that the SO₃ alone is the decisive factor for the development and speed of reaction. The other gases have no detectable effect here even if present in relatively high concentrations (40 to 50 mol%).

According to the kinetic theory on gas, the number of impacts of molecules from the reaction gas on a 1 cm² surface of the solid in 1 second can be calculated as

$$z = c_{\text{gas}} \cdot (kT/2m)^{1/2} \quad [\text{mole/cm}^2 \cdot \text{sec}] \quad (19)$$

For 550°C, the value for $z = 1.14 \cdot 10^{23}$ (mole/cm² · sec) when the concentration of the gas is $c_{\text{gas}} = 0.895 \cdot 10^{19}$ mol/cm³ in the test tube, the Boltzmanne constant k is $k = 1.38 \cdot 10^{-16}$ erg/grad and a mean molecular mass $m = 11.3 \cdot 10^{-23}$ g.

In a comparison with the reaction measured, in which the reaction rate k has to be entered in the same dimension (between $1.2 \cdot$ and $700 \cdot 10^{15}$ mole/cm² · sec), a collision exchange yields $\epsilon = k/z$ of about 10^{-6} to 10^{-8} for the reaction of the SO₂-O₂ mixture and of about 10^{-5} to 10^{-6} for the reaction of SO₃ with NaCl or CaCl₂. Thus, only a very small portion of the collisions result in reaction. This portion lies at a range which is higher by 1 or 2 powers of ten for the simpler bimolecular reaction of SO₃ as compared to the trimolecular reaction of solid substances with SO₂-O₂.

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